Continental J. Environmental Sciences 2: 12 - 16, 2008

TOXICITY ASSESSMENT OF HEAVY ELEMENTS IN RIVER SEDIMENTS USING ENERGY DISPERSIVE X-RAY FLUORESCENCE TECHNIQUE

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ABSTRACT
Trace quantities of thirteen elements have been determined from the aquatic sediments, of the Kubanni River- principal water way at Zaria, Nigeria. Energy Dispersive X-ray Fluorescence (EDXRF) Technique was used in determining Si,Ca,K,Ti,V,Fe,Co,Zn,Rb,Sr,Y,Zr and Nb in the sediments. An AXIL computer programme was used for the spectral analysis. The degree of pollution of the Kubanni River was ascertain and compared with the literature toxicity data. The Kubanni River sediments studied showed relatively low state of pollution for the elements determined and the River could still be used as a principal potable water source for Zaria inhabitants.

KEYWORDS: EDXRF, toxicity, heavy metals, River sediments, Kubanni

INTRODUCTION

Naturally occurring trace elements are deposited in aquatic environments either in the soluble form and eventually settle as bottom sediments along the course of the river (Hankouraou, 1998). The presence of these trace elements in aquatic environments is not without significance: for some of them are known to be very toxic and act as contaminants in the sediments. Man's activities have increased the loading of municipal and industrial contaminants to the nation's water ways. One of such water ways is the Kubanni River our study area in Zaria.

This river runs as a major principal drainage artery dissecting Zaria town. The increased loading of river beds with wastes could result in increased concentration of many heavy metal contaminants in sediments adversely affecting water quality and even the survival of aquatic organisms. Contaminants in sediments have a wide range of sources, and could be affected by lotic (running water), lentic (standing water), estuarine or lacustrine conditions, physical properties of sediments, the chemical state and biological composition of the water involved (Jenett *et al* 1980).

Most research in aquatic systems has been concerned with the form of contaminants present, rather than the amount of potential toxic material bound up in the sediments .The low concentration elements are undoubtedly the most difficult to study because background levels are always present in the environment masking their presence, and a small perturbation on an ecosystem could bring about rapid increase in the rates of synthesis of these heavy metals.

The potential impact of trace elements in sediments is determined here strictly with respect to the Kubanni River sediments. The detection of such elements requires sensitive and accurate analytical methods. In this work the Energy Dispersive X-ray Fluorescence (EDXRF) is chosen due to its reliability amongst other merits. This method of analysis offers an easy and sensitive way of determining any trace element in sediments. Its advantages include:

i) Simple sample preparation
ii) Non –destructive capability for analysis and
iii) Ability to determine many elements simultaneously.

EDXRF analysis suffers from certain set backs such as high investment, rigorous radiation protection, matrix effects, need for well trained personnel; thus limiting its application to few laboratories and research institutes such as the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, where this work was carried out.

This paper was a report on the analysis of some trace elements in the Kubanni river sediments by EDXRF technique.

The method was checked by analyzing United State Geology Survey (USGS) reference materials: USGS-AGV-1 (Analyzed Andasite) and USGS-G2 (Granite).

EXPERIMENTAL

In order to study the distribution of trace elements along the Kubanni River, 11sediment samples were collected at different locations (Fadama along Jos Road 5 samples and for Maje Road Bridge, Tudun Wada Bridge, Kano-Kaduna Bye-Pass Bridge, Zango Bridge, Ahmadu Bello University Dam and Kampangi Hills, one sample each). The 11 samples were collected in polyethylene containers .The distance between the sampling points is approximately 3 kilometers.

The sediments were allowed to dry in an oven at 50 ^{o} C for three days and were then homogenized, by manual grinding in agate mortar. The powder obtained after grinding was used for the preparation of pellets used for the analysis. A Mettler 100 CA digital balance was used for weighing the powdered samples, with only 2.0g of each sample required for the making of pellets. A cellulose binder polyvinylchloride (PVC) was added to each 2.0g of the sediments (powder) sample. The mixture was re-homogenized in agate mortar. The samples were then palletized (using the specac hydraulic press) by applying constantly a pressure of about 11.5 tones per cm^2. Pellets of 20 mm diameter and constant thickness of 5 cm were obtained from the samples.

Two standard reference materials were used for quality control measurements (USGS- AGV-1 and USGS-G2). Samples and standards were analyzed using the EDXRF facility of the Centre of Energy Research and Training (CERT), Ahmadu Bello University, Zaria Nigeria. The spectrometer consists of a Si(Li) detector, a preamplifier, amplifier and 4096 multi-channel analyzer.

X-rays emanating from two sources (^{109}Cd, ^{55}Fe) were used for the excitation of the characteristic K- lines of the analytes.

The non – linear least square fitting programme developed by IAEA and called AXIL was used for the determination of line intensities.

RESULTS AND DISCUSSION

Table 1 shows the average concentrations of the elements down-stream Kubanni River (Hankouraou, 1998).

Bowen (1979) had shown that Ca, Co, Fe, K, and Zn are probably essential to all plants. This could be of used to the seasonal crops grown at the Kubanni River basin. Elements like Si are essential to some groups, not necessary for all. Rb, K, Sr, and Ca are known to have a very high toxicity, which only arises when a large proportion of the essential ion has been replaced. Elements like Co are known to be very toxic to seed plants. Fe, V and Zn are moderately toxic while Ca, K, Rb and Sr are only toxic to very high concentration which was not the case with regard to Kubanni River. Zn is the element most frequently concerned with plant damage from industrial emissions, e.g.: on mine wastes, near smelters, sewage sludges, river dredgings, near galvanized steel buildings and where rubber tyres are burnt (Patterson, 1971). Excess of it inactivates soil enzymes (Bowen, 1979) and reduces the bacterial population (Griffiths, *et al* 1975), but does not have marked effects on the fauna. The Kubanni River level of zinc was found to be in the range 56 ppm to 665 ppm as shown in Table 1, which was less than 900 ppm an upper toxic limit for animals as given by (Jenett *et al* 1980) but can be toxic to plants according to Bowen (1979). Most of toxicity problems encountered with zinc are due to cadmium associated with zinc. As cadmium appears to be highly toxic to aquatic organism in the 0.02- 2.0 ppm

range, where a dose of 4 ppm in the diets of humans is normally considered to be toxic (Jenett *et al*. 1980). Some specified values have been accepted as the tolerated level in rivers. For example in Missouri the maximum allowed value as given by Jenett *et al.* (1980) was 150 ppm, while the Kubanni River mean value of zinc was obtained to be 149 ppm peaking up with the quoted value.

However, the results of this analysis show that the Kubanni River water might not pose any hazards and are quite suitable for drinking purposes if well treated.

The quality assurance results (Table2 and 3) shows that the determinations for most of the elements were in good agreement with the UGSG- AGV-1 SRM and UGSM-G-2 RSM literature values. The values of the relative errors ranged from 1 to 30% for most of the elements this is within the permissible limits (IAEA, 1988). For Co our results were too far from the recommended values of IAEA. The relative errors were 83% for USGS – AGV-1 and 133% for USGS-G-2, but they were within the values of the participants (Tran Van *et al*, 1989).

Table 1: Average concentrations of the elements detected in Kubanni River sediments. (Values in ppm otherwise as specified).

Elements	Mean value of the elements (Values in ppm or as stated) ±SD	Toxicity to plants by Bowen (1979) (in ppm)
Si%	30.3 (5)	
K%	2.0 (0.5)	
Ca%	0.4 (0.2)	
Ti%	0.5 (0.1)	
V	242 (220)	10 -40
Fe%	1.2 (0.1)	10-200
Co	<16.4 (5)	0.1 -3
Zn	149 (78)	60 - 400
Rb	118.2(5)	
Sr	69.0(8)	
Y	51.0 (20)	
Zr	884.2 (493)	
Nb	33.1(14)	

Table 2: Determination of Elemental Content of USGS- AGV-1 SRM (Values in ppm otherwise as specified)

Elements	Literature values	This work	Relative error%
Si%	27.4	25.1	8
K%	2.41	2.50	4
Ca%	3.53	3.71	5
Ti%	0.63	0.68	8
V	121	140	16
Fe%	1.60	1.60	0
Co	15.3	28.0	83
Zn	88.0	<86.7	
Rb	67.3	51.1	24
Sr	662	651	2
Y	20.0	15.4	23
Zr	227	227	0
Nb	15.0	<25.5	70

Table 3: Determination of Elemental Content of USGS G-2 SRM (Values in ppm otherwise as specified)

Elements	Literature values	This work	Relative error%
Si%	32.2	32.0	1
K%	3.71	3.58	4
Ca%	1.40	1.28	9
Ti%	0.28	0.20	29
V	36.0	36.5	1
Fe%	1.60	1.11	31
Co	4.60	<10.7	133
Zn	86.0	86.0	0
Rb	170	170	0
Sr	478	495	4
Y	11.0	12.2	11
Zr	309	309	0
Nb	12.0	12.0	0

CONCLUSION

The application of EDXRF technique in this work has been successful in the determination of elements from the Kubanni River sediments. Most of the elements identified are heavy metals of environmental concern. The elements determined were: Si, Ca, K, Ti, V, Fe, Co, Zn, Rb, Sr, Y, Zr and Nb. Only V, Fe, Co and Zn fell within the plants toxic limits as reported by Bowen (1979).Analysis of various crops during the irrigation period will give a clear indication of plants that could be affected by the mentioned contaminants. The toxicity levels of all the elements were found tolerable, showing that the river water can be used for drinking purpose if well treated.

ACKNOWLEDGEMENT

The Center of Energy Research and Training (CERT) and IAEA are hereby acknowledged for making all the facilities available and the AXIL programme respectively.

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Received for Publication: 07/09/2008
Accepted for Publication: 15/10/2008

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